III. "On Certain Ternary Alloys.   Part IV.   On a Method of Graphical Representation (suggested by Sir G. G. Stokes) of the way in which certain Fused Mixtures of Three Metals divide themselves into Two different Ternary Alloys; with further Experiments suggested thereby." By C. R. ALDER WRIGHT, D.Sc., F.R.S., Lecturer on Chemistry and Physics in St. Mary's Hospital Medical School; C. THOMPSON, F.I.C., F.C.S.; and J. T. LEON, B.Sc., F.C.S., Assistant Lecturer on Physics and Demonstrator of Chemistry in St. Mary's Hospital Medical School. Received January 29, 1891.

A method of graphically representing the results of the experiments described in the previous portions of these researches has been kindly suggested to one of us by Sir G. G. Stokes, founded on a principle which he regards as self-evident.   We subjoin a note which he has been so good as to draw up for us, explaining the application of this method, and then describe some further experiments which we have instituted with a view to test the correctness of the assumed principle.

Note on a Graphical Representation of the Results of Dr. Alder Wright's Experiments on Ternary Alloys.   By Sir G. G. STOKES, Bart., F.R.S.

Suppose three liquids such as water, ether, and alcohol, of which the third is miscible in all proportions with either of the others, are mixed together, the temperature being kept constant.   According to circumstances, the mixture forms a single liquid mass, or separates into two.   In the latter case, if we suppose that the liquids had been merely gently poured together, and imagine the upper and under portions separately to be homogeneous to start with, this state of things would not remain; an alteration of composition would take place close to the surface of separation on both sides, depending on the relative solubilities, &c., of the ingredients.   If now the two altered strata were mixed up with the rest of the portions to which they respectively belong, the same thing would go on again, and so on till a condition was reached in which what we may call an equilibrium of composition on the two sides of the surface of separation had been attained.   As this equilibrium depends only on the molecular forces, which are insensible at sensible distances, it is evident that the equilibrium would not be disturbed by removing a part of either the upper or the under liquid, or by adding to it liquid of exactly the

same composition as itself. This final state would take place only very slowly in the manner conceived above; but if the mixture be well agitated the total surface of separation, where alone the change of composition can go on, is greatly increased, and, moreover, the altered strata are mixed up with the rest of the liquids to which they respectively belong, so that the final state is reached comparatively quickly. I think I have seen an experimental verification of this anticipation, namely, that equilibrium depends only on the compositions of the upper and lower mixtures, and not on their quantities, in a French serial, but I have not the reference.

The same principles would apply to ternary alloys, which form a homogeneous mass, or separate into two, as the case may be; but of course the difficulty of preserving a constant temperature is much greater, as well as that of giving sufficient agitation to bring about the final condition.

It seemed to me that, for giving an insight into the results of experiments with ternary alloys, a mode of graphical representation might be usefully employed which is already well known. It is the same as that which Maxwell used for the composition of colours, at least with one slight addition. In this way the whole of the circumstances of the experiment, so far as they are material, would be exhibited to the eye.

Let A, B, C be three liquids, such as water, ether, alcohol, or else lead, zinc, tin, in fusion, of which the third (which for distinction may be called the solvent) may be mixed in all proportions with either the first or the second. Take a triangle, ABC (fig. 1), which may be of

FIG. 1.
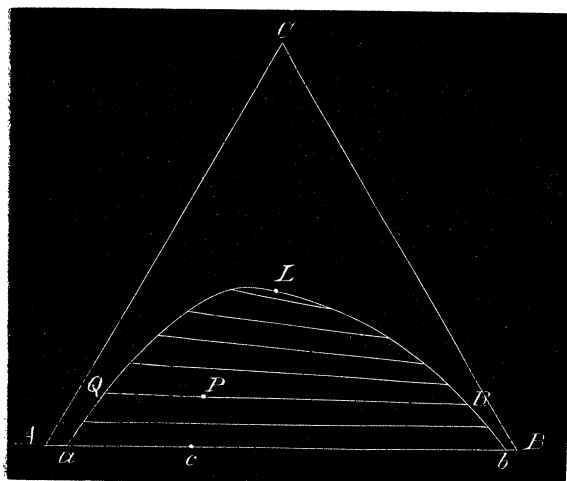
any form, but is most conveniently chosen equilateral; and, to represent the composition of any mixture of the three, imagine weights equal to those of the substances A, B, C placed at the points A, B, C, and find their centre of gravity, P.   To each different set of proportions A : B : C (the letters here denoting weights) will correspond a different position of P, which point will serve to represent to the eye the composition of an actual or ideal alloy (supposing the substances to be metals) formed of the three metals in the given proportions. If the quantity of the solvent be sufficient, P will represent on the diagram the composition of an actual alloy.   If it be insufficient, the alloy represented as to composition by P will be ideal only; and on attempting to form it the mass will separate into two layers.   If we suppose the agitation to have been sufficient, there will be equilibrium of solution at the surface of junction, and the mass will have reached its final state.   Supposing this condition to have been attained, let the two portions be analysed, and the points Q, R representing their compositions be laid down on the diagram, and joined by a straight line.   From the construction, this line must pass through the point P if there has been no loss by volatilisation or oxidation.   Let the same thing be done for several other proportions of the ingredients. Then the points Q, R will lie in a curve aQLRb, cutting AB in two points a, b, which represent, the first, a saturated solution of B in A, the second, a saturated solution of A in B.   Call this curve the *critical curve*, and the lines such as QR *tie-lines*, or simply *ties*.   Then the critical curve and the system of ties will represent the complete result of the experiments, supposing them to have been exactly made. Alloys of a pair may conveniently be called *conjugate*.   Intermediate tie-lines may be interpolated by eye; or if we prefer we may substitute for the system of ties their envelope, on which plan the result of the experiments would be completely represented by two curves, the critical curve and the envelope.

The critical curve separates mixtures of which alloys can actually be formed from those on attempting to form an alloy of which the mass separates into two layers.   In the latter case, if through P we draw a tangent to the envelope, cutting the critical curve in Q, R, the points Q, R will represent the compositions of the portions into which the mass separates, while their weights will be as PR to PQ.

If L be the limiting position of the chord QR, or, in other words, the point of contact with the critical curve of a common tangent to it and the envelope, as P tends to coincide with L, the two strata into which the mass separates tend to become identical in nature.   If we take a mixture of A and B, represented by a point c in ab, and continually increase the quantity of C from 0, the point P will ascend from c towards C until it reaches the critical curve.   At this stage the quantity of the second alloy has just dwindled away to nothing,

its nature, so long as there was any of it left, differing from that of the other alloy. If, however, the point *c* lies in the line CL, on increasing the quantity of C the two alloys merge into one.

On communicating to Dr. Alder Wright this mode of graphical representation, he tried it on a large scale on the results of two pairs of series from the former experiments. In one pair the temperature was 650°, and the proportion by weight of zinc to lead was 2 to 1 in the first case, and 1 to 2 in the second. In the other pair the weights of zinc and lead were equal, and the temperature 650° in one case and 800° in the other. In the first pair the agreement of the critical curves was very good, but the agreement in the direction of the ties was not by any means equally good. In the upper part of the figure, corresponding to the case in which there was a considerable quantity of tin, though not enough by any means to prevent the formation of two layers in the entire mass, the difference of inclination ranged to about 5°, the ties in the first case being inclined to those in the second as if they had been turned round in the direction of a line passing through the lead corner of the triangle, and turning round in the direction from lead-zinc to lead-tin. In the second pair of series in which the weights of lead and zinc were equal, and the temperature was 650° in the first case and 800° in the second, the critical curve for 800° was of the same general character as that for 650°, but lay a little inside it, which is just what was to be expected, on account of the increase of solubility attending the higher temperature. Moreover, the critical curve for 650° agreed very fairly with those for the same temperature in the first pair, notwithstanding the difference in the proportion of lead to zinc in the three cases.

I had not anticipated the greater accordance existing between the critical curves in different cases for the same temperature than that shown in the direction of the ties. But, when the plottings revealed it, it seemed to me that the cause was not far to seek. When the molten mass has as yet been but slightly stirred, the superposed alloys, supposed to be severally homogeneous, will most likely be represented on the diagram by points, one or both of which lie outside the critical curve. In this condition an alloy represented by an external point, having the metal C to spare, will be capable of dissolving bodily a portion of the other. This process accordingly, being something analogous to the solution of a salt till saturation is obtained, will go on as the stirring proceeds, and be sensibly complete in a moderate time. The two alloys will then be represented by two points lying on the critical curve. Such alloys may be said to be *associated*. But the passage from merely associated to truly conjugate alloys, as the stirring proceeds, is likely to be decidedly slower. For now neither alloy can bodily dissolve any portion, however small, of

the other; there can only be an interchange of constituents across the surface of separation.

The critical curve may be otherwise defined as the curve expressing the saturation of the solvent C with a mixture in given variable proportion of the remaining substances A, B. That it is really such, a little consideration suffices to show. The determination accordingly of the critical curve furnishes us with definite information, even though we do not go into the ulterior question of the condition of conjugation.

Perhaps the attainment of true conjugation might involve more stirring than would be practically feasible with molten metallic mixtures. The most hopeful way would seem to be to fuse the mass at a higher temperature than that intended for the experiment, stirring it well, and then let down the temperature to that intended, stirring all the time, and avoiding too rapid a fall of the temperature.

If truly conjugate alloys were obtained, and portions of each were taken and fused together at the temperature at which the alloys were made, the compositions ought to be the same as before. But if the alloys were merely associated, then, even if the stirring in the second part of the experiment were sufficient to ensure conjugation, the compositions would not be the same as the original, nor would they be independent of the proportion of the two alloys which the operator took for fusing together.

The triangular method of representation described by Sir G. G. Stokes in the above note obviously possesses several advantages, inasmuch as it represents in one diagram simultaneously a number of results which the ordinary curves drawn with abscissæ and ordinates can only partially indicate, consequently necessitating several different curves being drawn in order to represent graphically the entire set of results; thus the two branches of the "critical curve," obtained by directly plotting the figures yielded on analysis of the lowest and uppermost portions respectively of the compound ingot formed (in the case of a mixture separating into two different ternary alloys), represent the two solubility curves (*e.g.*, of zinc in lead-tin and of lead in zinc-tin), whilst the "ties" or "tie-lines" indicate, according as they slope to one side or the other, the relative proportions of the "solvent" (*e.g.*, tin) in the heavier and lighter alloys; so that, when (as in the case of mixtures of lead, zinc, and tin) with certain proportions of "solvent" the heavier alloy, and with other proportions the lighter one, contains the larger percentage, this variation is at once indicated to the eye by the change in direction of slope of the tie-lines (compare fig. 3). Further, when once the critical curve for a

given temperature has been laid down, it is at once evident by inspection whether a given mixture of metals will furnish a "real" alloy (not separating into two different ternary mixtures), or only an "ideal" alloy (*i.e.*, one not capable of existence, and consequently separating into two different ternary alloys) ; for, in the one case, the centre of gravity of the weights of the three metals respectively placed at the angles of the triangle will fall outside, and, in the other case, inside, the space enclosed between the critical curve and the base of the triangle.

Again, any abnormal results due to the formation of definite chemical compounds (such as the silver-zinc compounds $AgZn_5$ and Ag_4Zn_5, shown to exist by the experiments described in Parts II and III) are equally indicated by the irregularity of the outline of the critical curve deduced : thus fig. 2 indicates on Sir G. G. Stokes's

Fig. 2.
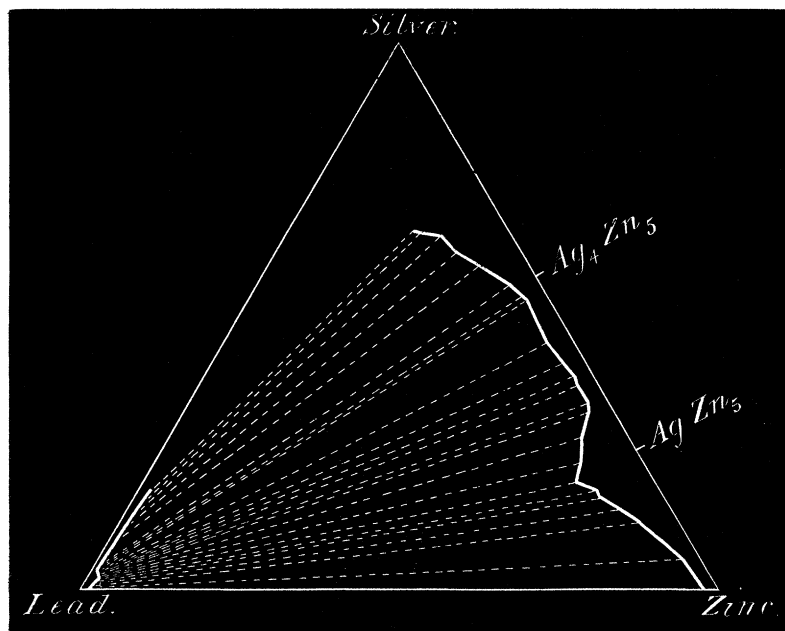
system some of the results obtained with zinc-lead-silver alloys (Part II, ' Roy. Soc. Proc.,' vol. 48, p. 33, Series I) ; the branch of the critical curve corresponding with the lighter alloys obviously indicates the first maximum of dissolved lead (at a point near to that corresponding with AgZn), the subsequent fall, and the point where marked increment again becomes apparent (near that corresponding

with Ag₄Zn₅) in the same way as the abscissa and ordinate curve shown in fig. 5, Part II, p. 35. It is noteworthy, however, that whilst the direction of the slope of the ties indicates that throughout the lighter alloy contains more silver than the heavier one, the triangular graphical representation does not clearly indicate that the difference in silver percentage between the lighter and heavier alloys rises to a maximum and then diminishes again, as is distinctly shown by the ordinary method with abscissæ and ordinates, as depicted in fig. 4, Part II, p. 35.* Precisely the same remarks apply if the analogous results obtained with bismuth-zinc-silver alloys described in Part III are similarly plotted.

In addition, however, to the employment of this improved method of graphical representation, Sir G. G. Stokes deduces from *a priori* considerations an important general principle, viz., that when a sufficient amount of intermixture of the constituent metals has taken place a state of equilibrium is arrived at (the temperature being constant throughout), such that the presence of one ternary alloy in no way affects the composition of the other; so that the addition or subtraction of a further quantity of either alloy, or of any mixture of the two, does not affect the compositions, but only the relative quantities present, of the two alloys; whence, if any given weights of the two fused alloys be intermixed, the same weights of the same alloys will separate again from one another by gravitation on standing. If, therefore, two given alloys, A and B, be thus related (truly *conjugate*), and in any particular experiment carried out until equilibrium is reached one of these alloys, A, be formed, the other alloy, B, must necessarily be also produced; and this must be the case no matter what may have been the relative proportions subsisting between the three metals in the mixture originally employed.

It appeared to us of considerable interest to examine from the experimental point of view whether this general principle can be

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* [Sir G. G. Stokes has pointed out to me that the diagram, fig. 1, shows at once that, inasmuch as the difference between the percentages of the solvent in two conjugate alloys vanishes for the pair, *a, b,* being *nil* for each, and again for the pair which merge into one, represented by the point L, it must necessarily be a maximum for some intermediate pair; and also that, in order to preserve the continuity of conditions, we must, in crossing L, pass from the upper alloy to the lower, and *vice versâ.* Hence, if the entire system of ties could be determined, so as to obtain every possible pair of conjugate points lying, one on one side, the other on the other side, of L, and if these values were plotted on the abscissa and ordinate system, the curve representing the difference between the percentages of the solvent, after having ascended and attained a maximum elevation, must descend again to the base line at a point corresponding with L. If we wish to continue the curve beyond that point, we must now take the ordinates negative instead of positive, the same in magnitude as before, and the curve having crossed the base line, and attained a minimum elevation, will ultimately ascend again to the final point on the base line.—C. R. A. W., February 25, 1891.]

verified in practice, or whether interfering causes prevent anything
more than demonstrations of approximate correctness being obtained;
the more so that some of the results previously obtained by two of us
do not appear to be in harmony with Sir G. G. Stokes's proposition.
In Part I ('Roy. Soc. Proc.,' vol. 45, p. 461) three series of experi-
ments were described, made with lead, tin, and zinc, where the ratio
of lead to zinc was 2 to 1, 1 to 1, and 1 to 2, in the three series
respectively; and the figures obtained led us to the conclusion that
" whilst an indefinite number of different mixtures may be prepared,
each one of which will give the same heavier alloy, the lighter alloy
simultaneously formed will be different in each case; and conversely:"
a deduction obviously incompatible with Sir G. G. Stokes's proposition.
On the other hand, it is argued by Sir G. G. Stokes that these experi-
ments do not necessarily prove anything more than the extreme
difficulty experienced whilst making experiments with fused metals
in obtaining such an intimate intermixture as to bring about the
condition of perfect equilibrium between the two alloys formed in
any given instance; and that, in point of fact, the differences
observed in the compositions of the various lighter alloys associated
with a given heavier one, or *vice versâ*, are not greater than might
reasonably be expected were equilibrium not perfectly attained in
some or all of the observations. Further, the fact that the differences
are *always in the same general direction* tends to indicate that some
constant interfering cause is at work; thus, when curves were
plotted (Part I, fig. 5, p. 476) with the tin percentages in the heavier
alloys as abscissæ, and the excesses of tin percentage in the lighter
alloys over those in the heavier ones as ordinates, the curve deduced
from the series of experiments where the ratio of lead to zinc in the
original mixture of metals was 2 to 1 *underlay* that similarly obtained
in the second series, where the ratio was 1 to 1, which again *underlay*
that deduced from the third series, where the ratio was 1 to 2;
whereas all three curves should have coincided were Sir G. G. Stokes's
proposition correct, and all interfering causes completely eliminated.

An analogous result is obtained when the analytical figures are
plotted on Sir G. G. Stokes's triangular system. Fig. 3 represents
the plottings thus obtained of the two series where the ratio of zinc
to lead was 2 to 1 and 1 to 2 respectively (Part I, 'Roy. Soc. Proc.,'
vol. 45, Series IV, p. 474, and Series VI, p. 475) the temperature
throughout being near to 650°. The ties in the first case are indi-
cated by dotted lines, and in the second by continuous ones.
Obviously the critical curves deduced from the two sets of observa-
tions respectively do not differ very markedly; but the angles of
slope of the ties are not identical, so that a given heavier alloy is not
conjoined with the same lighter one (nor *vice versâ*) in the two cases;
whilst the direction of the variation is the same throughout.

Fig. 3.
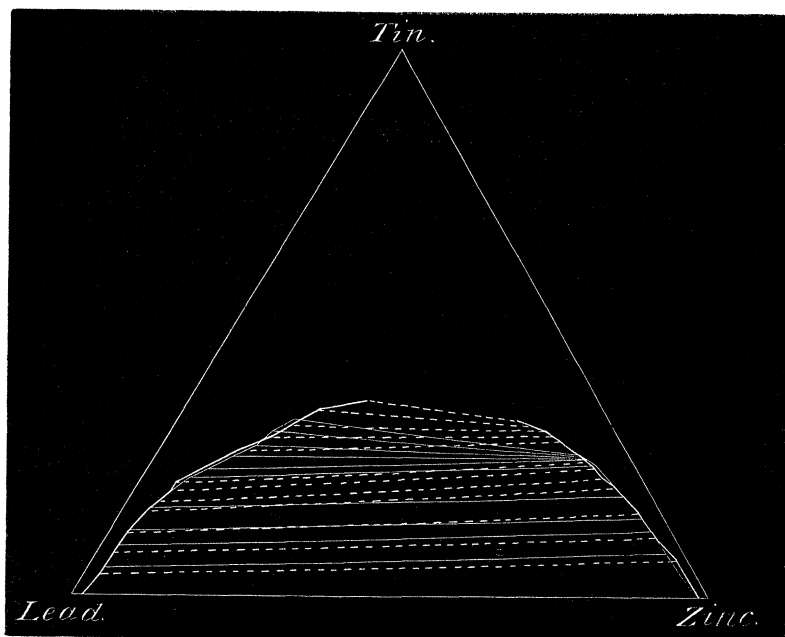
In order, if possible, to obtain experimental evidence of the truth
or otherwise of the general proposition arrived at by Sir G. G. Stokes,
as well as some explanation of the deviation therefrom of these
previous results, we first of all carried out various further experi-
ments with mixtures of lead, zinc, and tin, employing additional
precautions to minimise errors due to imperfect intermixture, more
especially by continuing for much longer periods of time the process
of agitation of the fused metals by vigorous stirring; the results,
however, did not differ materially from the previous ones, and
indicated generally that the composition of the heavier alloy
practically obtained associated with a given lighter one, or *vice versâ*,
was subject to fluctuation within certain not very wide limits,
according to the proportion subsisting between lead and zinc in the
original mixture employed; but whether this result was brought
about by interfering causes, or was possibly due to the not absolute
correctness of Sir G. G. Stokes's principle, the experiments did not
enable us to decide.   In the hope of eliminating disturbing causes,
we next endeavoured to carry out analogous observations at the
ordinary temperature with liquids not metallic in their nature, but
resembling the metals tin, lead, and zinc from the point of view of

their relative solubilities, *i.e.*, two of the liquids being only miscible together to limited extents (like lead and zinc), whilst the third was miscible in all proportions with either of the others separately. The difficulty of making sufficiently accurate analyses of the ternary mixtures thus obtained prevented our using several such groups of liquids, which at first sight suggested themselves, more particularly mixtures of *alcohol, water, and ether;* but we found that *chloroform, water, and glacial acetic acid* fulfilled all the necessary conditions; so that, when a mixture of equal weights of the first two with not too large a proportion of the third was well agitated and allowed to stand, it separated into two ternary solutions exactly correlative with the ternary alloys previously examined; the heavier one consisting chiefly of chloroform with some of the acetic acid and an amount of water proportionate to the acetic acid present; the other consisting mainly of water with the rest of the acetic acid, and more or less chloroform dissolved therein. Calling any given such pair of conjugate mixtures A and B respectively, we found that *the general principle deduced by Sir G. G. Stokes could be verified with sensible accuracy with these liquids;* on agitating together A and B in various proportions, *each liquid separated out again unchanged in each case, no matter whether* A *was used in large excess of* B, *or vice versâ.* On the other hand, when two different alloys, A and B, were made of lead, tin, and zinc in such proportions that one was approximately conjugate to the other as indicated by the previously recorded observations, we did not succeed in getting anything like such sharp results; experiments where 2 parts of A to 1 of B were mixed together, and treated side by side with a mixture of 1 part of A to 2 of B, did not give quite the same results in the two cases, the differences being considerably larger than anything attributable to errors of analysis and such like sources of inaccuracy.

Mixtures of Chloroform, Water, and Acetic Acid.

The analysis of such mixtures we found could be carried out with considerable accuracy and ease in the following way; a weighed portion of the mixture (contained in a stoppered bottle) was diluted with water, and titrated with a fresh caustic soda solution accurately standardised, using phenolphthaleïn as indicator. Another portion, weighed in a flask or bulb tube containing a little water, was then submitted to the action of a current of dry air sucked through it, the issuing gases and vapours being made to pass through a pumice-stone and sulphuric acid drying tube. When constancy of weight was attained, and all chloroform had been removed, the loss of weight of the entire apparatus represented the chloroform; whilst the gain in weight of the apparatus (as compared with its weight before intro-

ducing the mixture) represented the water and acetic acid jointly, from which the water was obtainable by subtracting the weight of acetic acid deduced from the previous titration. A number of preliminary experiments showed that the sulphuric acid drying tube sufficed to retain all traces of acetic acid carried away by the current of air, whilst, on the other hand, it did not permanently absorb chloroform, and did not sensibly act on the chloroform so as to break it up, or hydrolyse it into hydrochloric and formic acids, &c.

As a first experiment, we thought it desirable to find out how short a time might be requisite to bring about such a condition of equilibrium (after vigorous agitation) that no sensible further alterations took place in the composition of the two liquids formed. We found that agitation for a minute or two at a time at intervals for a period of an hour always sufficed to bring about this state of matters. Thus, the following numbers were obtained in one set of observations, the liquids being contained in a well-stoppered stopcock-reservoir, so that the lower liquid could be readily sampled by opening the stopcock, and the upper one by means of a pipette. The original mixture contained—

$$\begin{array}{ll} \text{Chloroform} \dots\dots\dots\dots\dots & 30\cdot0 \text{ per cent.} \\ \text{Water} \dots\dots\dots\dots\dots\dots & 29\cdot7 \quad ,, \\ \text{Glacial acetic acid } (C_2H_4O_2) & 40\cdot3 \quad ,, \\ \hline & 100\cdot0 \end{array}$$

	Bottom fluid.			Top fluid.		
	Chloro-form.	Water.	Acetic acid.	Chloro-form.	Water.	Acetic acid.
Agitated at intervals for 1 hour: allowed to stand 1 hour more.	..	..	21·21	..	..	48·08
Next day (about 18 hours afterwards) ..	75·53	3·18	21·29	10·50	40·96	48·54
Agitated at intervals for a week: allowed to stand 2 hours since last agitation..	75·68	3·04	21·28	10·53	40·94	48·53

Analogous figures were obtained in several other similar experiments, the differences observed after different periods being but small (much less than 1 per cent.), and obviously due to experimental

errors, more especially slight variations of temperature; but with imperfectly intermixed fluids differences of much greater magnitude were often observed.

Next we prepared a series of mixtures containing as nearly as possible equal weights of water and chloroform with varying proportions of acetic acid up to 50 per cent. of the last. This amount produced a single homogeneous fluid not separating into two liquids, whereas with 45 per cent. separation readily occurred. The following average numbers were obtained from about twenty experiments :—

Percentage of acetic acid originally used.	Bottom fluid.			Top fluid.			Excess of percentage of acetic acid in top fluid over that in bottom.
	Chloroform.	Water.	Acetic acid.	Chloroform.	Water.	Acetic acid.	
0	99·01	0·99	0	0·84	99·16	0	. .
4·0	98·24	0·72	1·04	0·92	92·62	6·46	5·42
10·9	94·98	1·19	3·83	0·79	81·52	17·69	13·86
16·5	91·85	1·38	6·77	1·21	73·69	25·10	18·33
19·2	91·23	0·82	7·95	1·85	70·42	27·73	19·78
24·6	87·82	1·13	11·05	2·97	63·32	33·71	22·66
35·2	80·00	2·28	17·72	7·30	48·58	44·12	26·40
42·6	72·86	3·62	23·52	12·82	37·82	49·36	25·84
44·9	70·13	4·12	25·75	15·11	34·71	50·18	24·43

These figures clearly show the close analogy between mixtures of chloroform, water, and acetic acid, and such ternary metallic mixtures as lead-zinc-tin, bismuth-zinc-silver, &c. On plotting curves as with the alloys previously described, the following results are deducible :—

1. Plotting percentages of acetic acid in one mixture (the lighter one, for example) as abscissæ, and excesses of percentages of acetic acid in top over those in bottom fluids as ordinates, the curve indicated in fig. 4 is obtained, closely resembling in general features those obtained with lead-zinc-silver and bismuth-zinc-silver alloys, the curve ascending to a maximum elevation and then coming partly down again, but not so much so as to descend again to the base line.

2. Percentages of acetic acid in heavier liquids as abscissæ, and those of water as ordinates. Curve shown in fig. 5, representing the *solubility of water in chloroform in presence of acetic acid.*
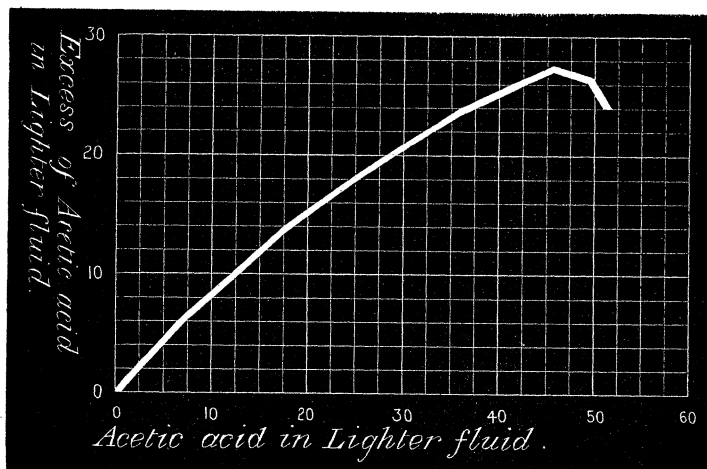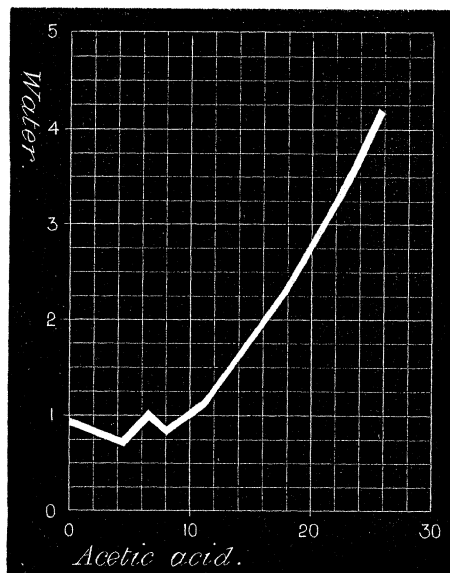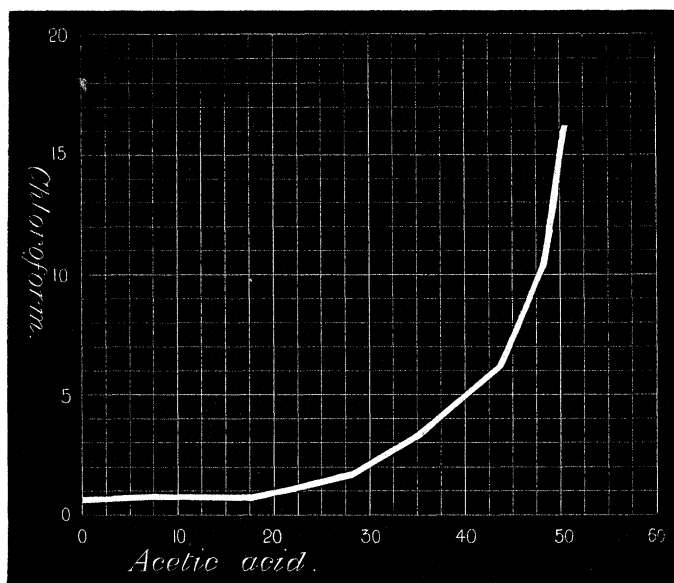
FIG. 4.

FIG. 5.

3. Percentages of acetic acid in lighter liquids as abscissæ, and those of chloroform as ordinates.   Curve shown in fig. 6, representing the *solubility of chloroform in water containing acetic acid.*

FIG. 6.

These two solubility curves closely resemble those of the metals in general features, rising upwards at an accelerating rate, so that the curves are somewhat concave upwards.

Fig. 7 shows the same results plotted in accordance with Sir G. G. Stokes's triangular method of graphical representation, the two branches of the critical curve being represented by the continuous lines, and the ties by the dotted lines.

The point P represents the mixture containing

$$\begin{aligned}
\text{Acetic acid} &\dots\dots\dots\dots\quad 50 \text{ per cent.} \\
\text{Water} &\dots\dots\dots\dots\dots\quad 25 \quad ,, \\
\text{Chloroform} &\dots\dots\dots\dots\quad 25 \quad ,,
\end{aligned}$$

which, as above stated, was homogeneous, not separating into two different fluids; consequently P is a point *outside* of the space representing "ideal" mixtures bounded by the base line and the two branches of the critical curve. Just as in the case of fig. 2, the direction of slope of the ties obviously indicates that the lighter fluid always contained the larger proportion of acetic acid; but the variation in the difference between the proportions of acetic acid in the two fluids is not so clearly indicated as by the ordinary method of plotting shown in fig. 4, where the difference in acetic acid percentage between the two fluids visibly attains a maximum and then decreases.

Fig. 7.
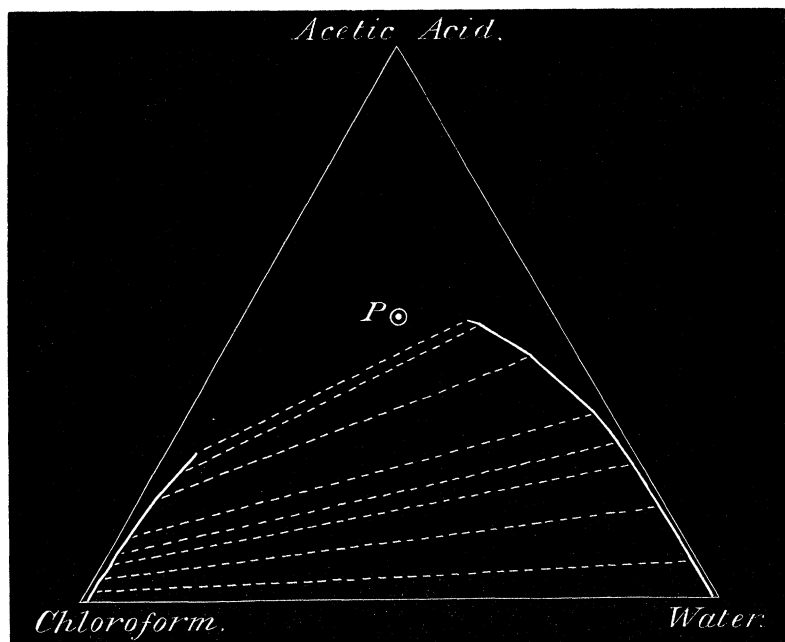
We next prepared various mixtures of chloroform, water, and acetic acid in known proportions, agitated them thoroughly together, and, by means of a separating reservoir, drew off into separate vessels the heavier and lighter portions.   Weighed quantities of these were then transferred to stoppered vessels, and again well agitated together at intervals for some time.   After again separating by standing, samples of the heavier and lighter_fluids formed were drawn off and analysed. The following figures wer   obtained in several such experiments :—

I. Equal weights of Chloroform and Water used, and Acetic Acid = 30 per cent. of the whole. The two conjugate mixtures formed were then agitated together in three different proportions, viz.:

(α.)   1 part of heavier liquid to 3·0 of lighter.
(β.)   1   ,,   ,,   1·6   ,,
(γ.)   1   ,,   ,,   0·5   ,,

	Chloroform.		Water.		Acetic acid.	
	Heavy liquid.	Light.	Heavy.	Light.	Heavy.	Light.
α.............	84·44	4·15	1·54	56·22	14·02	39·63
β.............	84·57	4·00	1·32	56·22	14·11	39·78
γ.............	84·24	4·10	1·46	56·25	14·30	39·65

Obviously in all three cases the compositions of the heavy and light liquids respectively are sensibly identical.

II. Equal weights of Chloroform and Water, and Acetic Acid = 19·5 per cent. of the whole.

(α.)   1 part of heavier liquid to 2·0 of lighter.
(β.)   1   ,,   ,,   1·33   ,,
(γ.)   1   ,,   ,,   0·5   ,,

	Chloroform.		Water.		Acetic acid.	
	Heavy liquid.	Light.	Heavy.	Light.	Heavy.	Light.
α.............	90·77	1·78	0·75	71·25	8·48	26·97
β.............	91·68	1·91	1·01	69·74	7·31	28·35
γ.............	91·23	1·87	0·70	70·24	8·07	27·89

III. Equal weights of Chloroform and Water, and Acetic Acid = 44·9 per cent. of the whole.

(α.)   1 part of heavy liquid to 3·3 of lighter.
(β.)   1   ,,   ,,   0·49   ,,

	Chloroform.		Water.		Acetic acid.	
	Heavy liquid.	Light.	Heavy.	Light.	Heavy.	Light.
α.............	70·46	15·13	3·97	34·92	25·57	49·95
β.............	69·82	15·08	4·29	34·62	25·89	50·30

In neither of these experiments is there any difference in composition observable to an extent greater than might readily be supposed to be due to experimental errors, including those caused by differences in laboratory temperature at different times whilst making the observations.

In the following two experiments only the acetic acid was determined :—

Parts of lighter liquid to 1 of heavier.	Acetic acid.	
	Heavy liquid.	Light.
IV. $\begin{cases} 2\cdot33 \\ 0\cdot56 \end{cases}$	21·28 21·28	48·53 48·38
V. $\begin{cases} 2\cdot0 \\ 1\cdot0 \\ 0\cdot5 \end{cases}$	5·76 5·44 5·54	22·27 22·77 22·35

Experiments with Approximately Conjugate Alloys of Lead, Tin, and Zinc.

The experiments above described most strongly suggest that when interfering causes are removed, so that the mixtures of liquids dealt with can sensibly attain a condition of equilibrium, truly conjugate pairs of mixtures are formed, as supposed by Sir G. G. Stokes, of such a nature that the two may be intermixed in any proportions without any alteration in composition being thereby caused. Presumably the chief interfering cause in the former experiments with lead, zinc, and tin lay in the difficulty of obtaining thorough intermixture by simply stirring vigorously in a hot crucible; it might, therefore, be expected that if, instead of stirring together the three metals melted *en masse*, they were divided into two fractions and separately melted in such proportions as to produce two masses of approximately the composition of a pair of conjugate alloys, and these alloys were then mixed together and well stirred, a nearer approximation to truly conjugate compositions might be attained. We tried several experiments in this direction, but the results were far less sharp and well defined than those obtained with chloroform, water, and acetic acid, where a much more thorough intermixture by agitation in a closed vessel could be readily effected.

Thus, in one set of experiments we first prepared two alloys of approximately conjugate composition for a temperature of about 800° (Part II, ' Roy. Soc. Proc.,' vol. 48, p. 29), viz. :—

	Tin.	Lead.	Zinc.
Heavier alloy	29·5	50·0	20·5
Lighter alloy	28·5	13·0	58·5

Two parts of the first and one of the second were then melted in two separate crucibles, and the contents of one crucible poured into the other, and well intermixed by vigorous stirring for some minutes; the whole was then poured into a red-hot narrow clay crucible, and maintained at near 800° for 8 hours in the lead bath. Simultaneously, a second clay test-tube was heated, containing a similarly prepared mixture of one part of the first alloy to two of the second. The compound ingots ultimately obtained were analysed with the following results, obviously showing much less close agreement than in the case of the chloroform, water, and acetic acid; moreover, the difference in tin percentage between top and bottom underwent changes in opposite directions to extents closely commensurate with those calculable from the values deduced in Part I for the differences in the curves obtained according as lead or zinc predominated in the original mass, or as the two were present in equal proportions.

	Heavier end.			Lighter end.			Excess of tin percentage in lighter over that in heavier.
	Tin.	Lead.	Zinc.	Tin.	Lead.	Zinc.	
2 parts of first alloy to 1 of second.......	30·16	47·09	22·75	26·39	11·41	62·20	−3·77
2 parts of second alloy to 1 of first.........	28·05	52·34	19·61	28·76	11·69	59·55	+0·71
Difference ..	+2·11	−5·25	+3·14	−2·37	−0·28	+2·65	4·48

Similarly, in two other sets of experiments, the following tin percentages were obtained, again showing a notable divergence in the results according as the heavy alloy was employed to doubl he extent of the lighter one, or only half.

	Heavier end.	Lighter end.	Excess in lighter end.	Heavier end.	Lighter end.	Excess in lighter end.
2 parts of first heavier alloy to 1 of lighter.	15·39	17·51	+ 2·12	23·45	23·39	− 0·06
2 parts of first lighter alloy to 1 of heavier.	15·07	19·56	+ 4·49	22·57	25·41	+ 2·84
Difference......	+ 0·32	− 2·05	2·37	+ 0·88	− 2·02	2·90

In every case the same general result is noticed, that when the two approximately conjugate alloys are intermixed in such proportions that lead predominates over zinc in the total mass, or *vice versâ*, the differences in tin percentage between the two ends of the compound ingots formed are of the same kind as those observed in Part I with original masses containing lead and zinc in different ratios : viz., that when lead predominates a point is obtained belonging to a curve *underlying* that pertaining to cases where zinc predominates : whence it appears pretty certain that, whatever the causes may be that prevent truly conjugate alloys from being obtained under the conditions of the one set of experiments (whether incomplete inter-mixture, or something else), they also operate in the other series of observations.

Taking into account, however, the fact that in the experiments with chloroform, water, and acetic acid truly conjugate mixtures were obtained when a sufficient amount of intermixture by agitation had occurred, *but not till then,* the final conclusion appears to be warranted *that the proposition set forth by Sir G. G. Stokes is a perfectly correct one,* and that the divergences noticed in certain of the alloy experiments are due to the inherent nature of the case as regards the difficulties in the way of obtaining sufficiently complete intermixture : possibly these difficulties might be overcome by enclosing the fused mixtures of metals in a stoppered vessel or crucible-flask of clay, and agitating this by long continued shaking about, whilst keeping it sufficiently hot in some kind of muffle furnace ; but the appliances at our dis-posal have not permitted us actually to decide this point experi-mentally. The difficulty of carrying out such experiments is further enhanced by the circumstance that metallic alloys, when intermixed by vigorous agitation, do not appear to separate again from one another anything like so readily as such substances as chloroform and water or ether and water; small vesicles or droplets of the heavier alloy remain suspended in the lighter one (and *vice versâ*) for long

periods of time, necessitating the maintenance of a nearly equable temperature, and the remaining at rest for many hours, before the top part of the mass becomes sensibly free from suspended portions of the heavier alloy, and the bottom part from similar portions of lighter alloy. The analytical numbers obtained on examining different layers of the compound ingots prepared in the experiments described in the earlier parts of these researches long ago convinced us of this ; but, in addition, an actual visible presence of suspended particles of one alloy in the midst of another, even after 8 hours tranquil fusion, may be often observed in the case of silver-lead-zinc and silver-bismuth alloys where the proportions of metals used are such as to form mixtures containing considerable amounts of Ag_4Zn_5 : by the aid of a lens, or even with the naked eye, red particles disseminated through a much lighter coloured matrix can often be distinguished on examining the central portions of an ingot that has been filed smooth and bright, and then kept for awhile so as to allow the red tinge to develop.

IV. " On the Structure of Amœboid Protoplasm, with a Comparison between the Nature of the Contractile Process in Amœboid Cells and in Muscular Tissue, and a Suggestion regarding the Mechanism of Ciliary Action." By E. A. SCHÄFER, F.R.S. Received January 26, 1891.

It has been shown by the researches of numerous histologists, of whom Heitzmann and Frommann, and, in this country, Klein, must be reckoned the pioneers, that the protoplasm of many cells exhibits the appearance of a network containing an apparently homogeneous material in its meshes. The network is known as the *reticulum* or *spongioplasm*, the clear material in its meshes as *enchylema* (Carnoy) or *hyaloplasm*. In many cells it is not difficult to observe this structure even without the addition of reagents, but in amœboid cells such as the white blood corpuscle and the amœba it is less obvious, and its presence has not been generally conceded. Recently, Professor Stricker[*] has published a photograph of an amœboid white blood corpuscle, taken instantaneously by aid of the electric light, which shows the reticular appearance in quite an unmistakable manner ; it must be granted, therefore, that the amœboid white blood corpuscle also has this structure.

Previously to the appearance of Professor Stricker's photograph, I had myself for some time been engaged in investigating the structure of amœboid cells with the aid of photography. Being unprovided
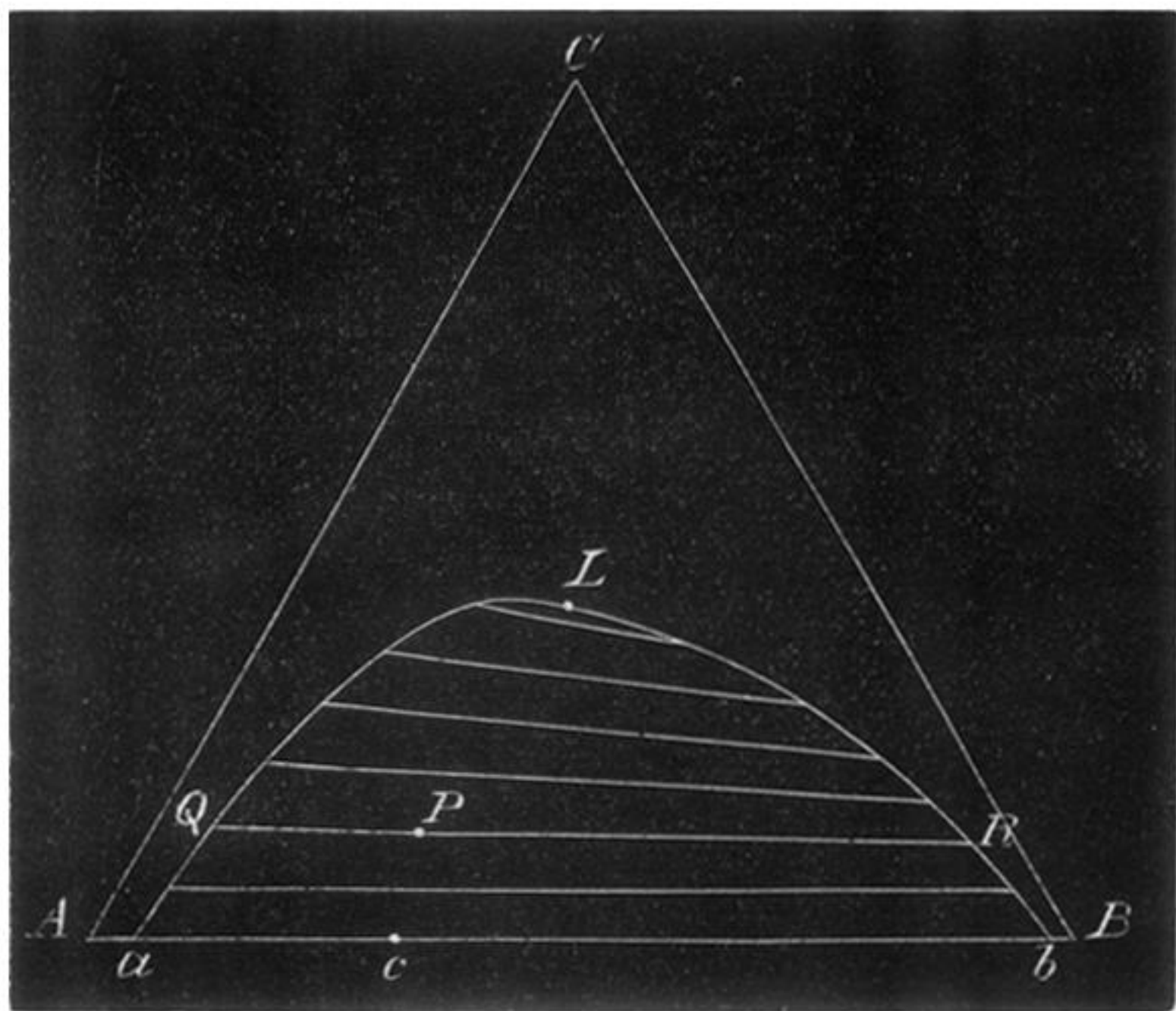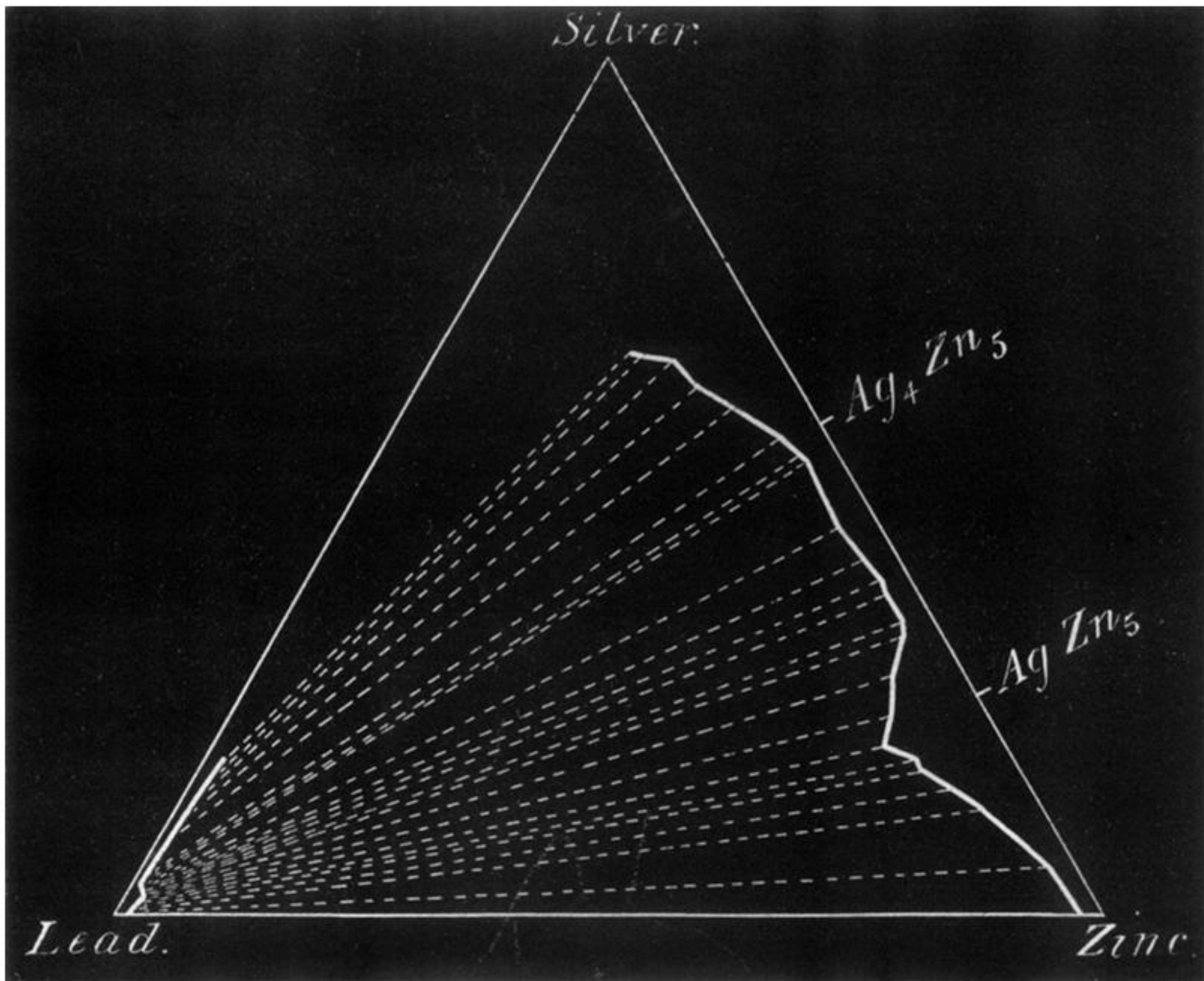
[*] ' Wiener Medic. Jahrb.,' 1890.
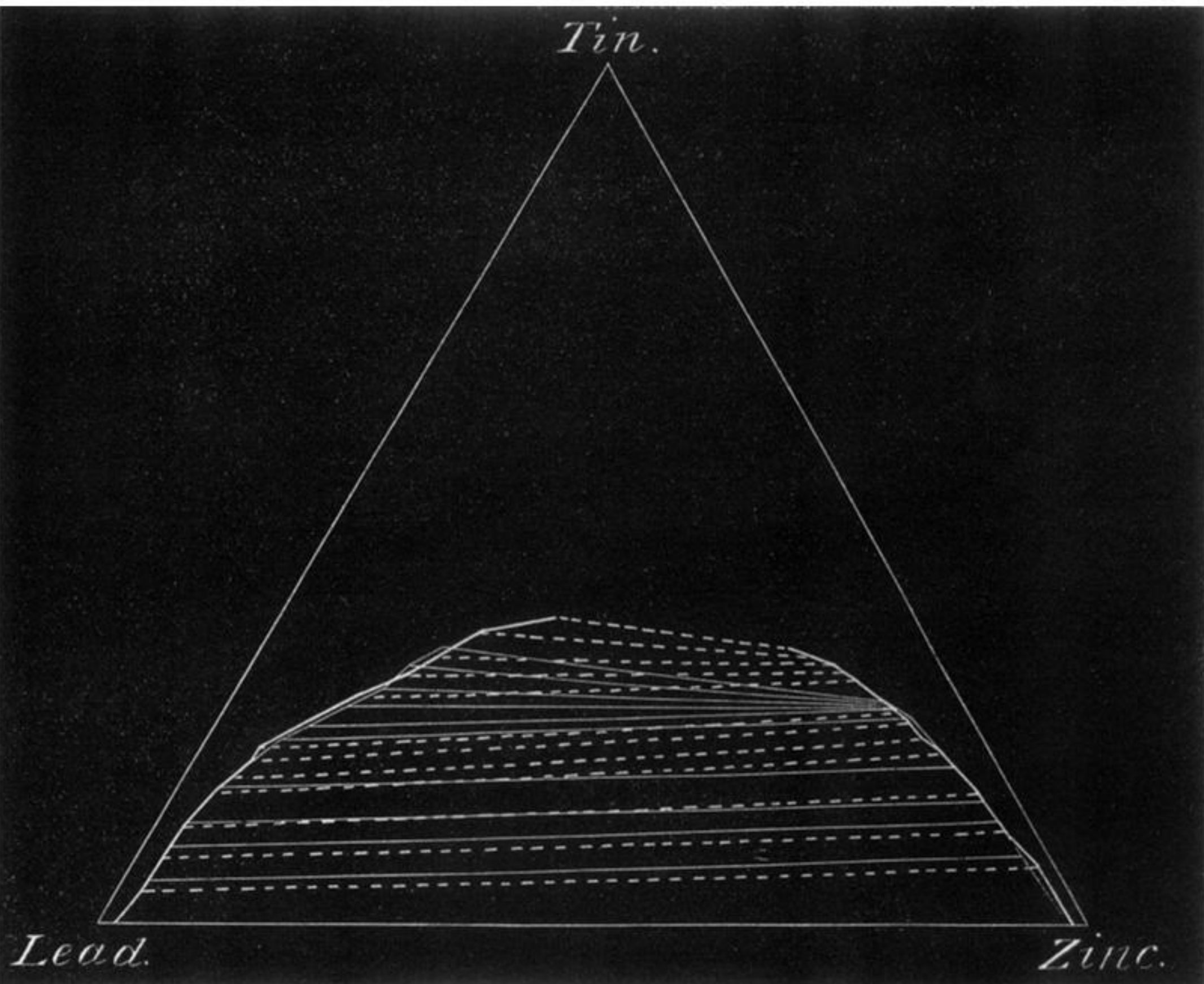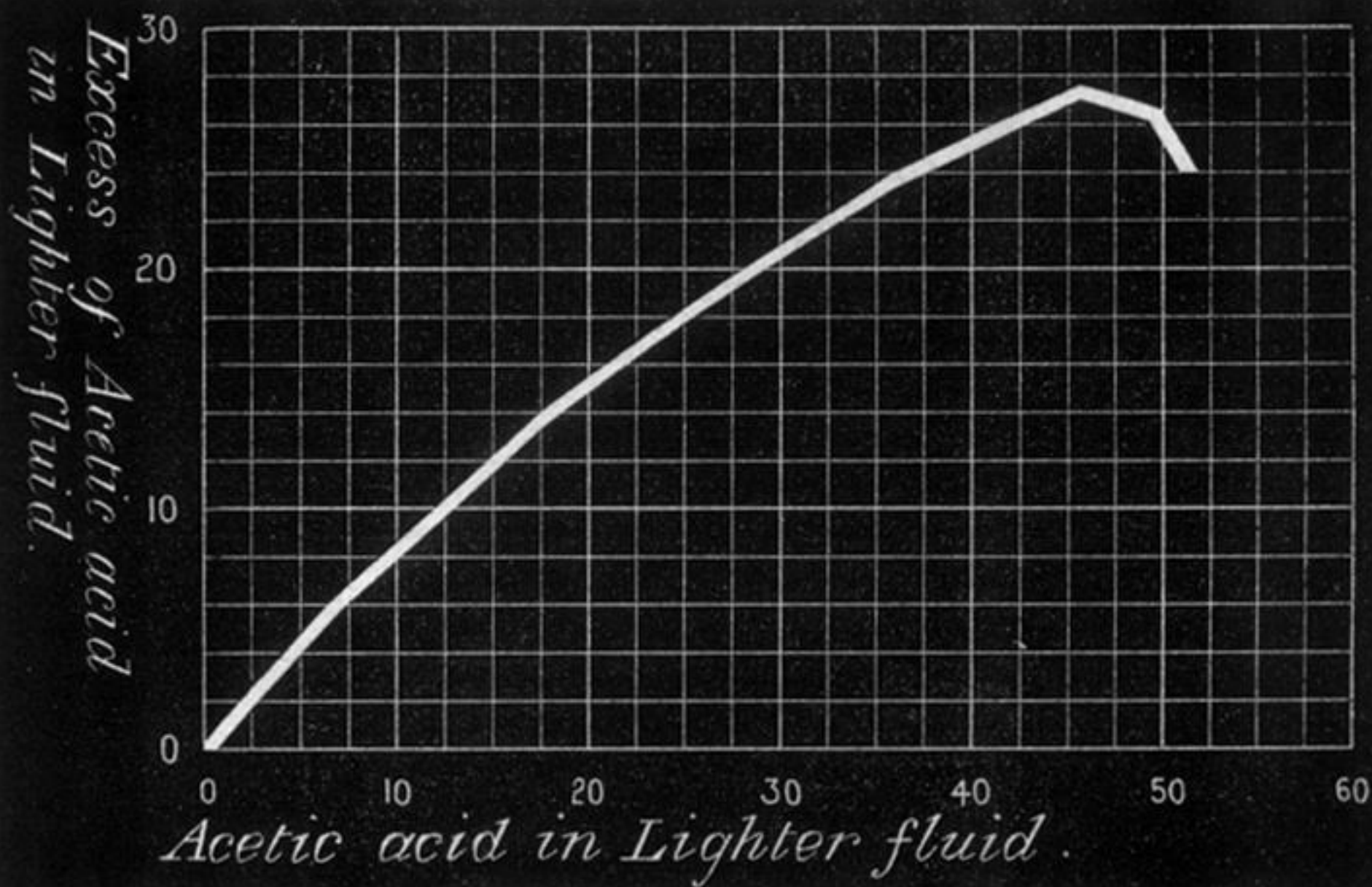
FIG. 1.

Fig. 2.

FIG. 3.

FIG. 4.

Excess of Acetic acid in Lighter fluid.

Acetic acid in Lighter fluid.

FIG. 5.

FIG. 6.

FIG. 7.